

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

REC'D 12 OCT 2005

(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference Cal 88163	FOR FURTHER ACTION See Form PCT/IPEA/416	
International application No. PCT/EP2004/006979	International filing date (day/month/year) 28.06.2004	Priority date (day/month/year) 03.07.2003
International Patent Classification (IPC) or national classification and IPC C10G47/14		
Applicant ENI S.P.A.		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input type="checkbox"/> <i>(sent to the applicant and to the International Bureau) a total of sheets, as follows:</i></p> <ul style="list-style-type: none"> <input type="checkbox"/> <i>sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</i> <input type="checkbox"/> <i>sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</i> <p>b. <input type="checkbox"/> <i>(sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)), containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</i></p>		
<p>4. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <input checked="" type="checkbox"/> Box No. I Basis of the opinion <input type="checkbox"/> Box No. II Priority <input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability <input type="checkbox"/> Box No. IV Lack of unity of invention <input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement <input type="checkbox"/> Box No. VI Certain documents cited <input type="checkbox"/> Box No. VII Certain defects in the international application <input type="checkbox"/> Box No. VIII Certain observations on the international application 		
Date of submission of the demand 25.01.2005	Date of completion of this report 11.10.2005	
Name and mailing address of the International preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Deurinck, P Telephone No. +31 70 340-2404	



INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/006979

Box No. I Basis of the report

1. With regard to the language, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
 - This report is based on translations from the original language into the following language, which is the language of a translation furnished for the purposes of:
 - international search (under Rules 12.3 and 23.1(b))
 - publication of the international application (under Rule 12.4)
 - international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the elements* of the international application, this report is based on (replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):

Description, Pages

1-6, 8-69	as originally filed
7	received on 04.05.2005 with letter of 03.05.2005

Claims, Numbers

1-25	received on 04.05.2005 with letter of 03.05.2005
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Drawings, Sheets

1; 2	as originally filed
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a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. The amendments have resulted in the cancellation of:
 - the description, pages
 - the claims, Nos.
 - the drawings, sheets/figs
 - the sequence listing (*specify*):
 - any table(s) related to sequence listing (*specify*):
4. This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
 - the description, pages
 - the claims, Nos.
 - the drawings, sheets/figs
 - the sequence listing (*specify*):
 - any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/EP2004/006979

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	4-7,10-13,17,19-25
	No:	Claims	1-3,8,9,14-16,18
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-25
Industrial applicability (IA)	Yes:	Claims	1-25
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/EP2004/006979

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following document:

D1: US 5 230 789

1. Lack of Novelty

1.1

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of independent **Claim 1** is not new in the sense of Article 33(2) PCT.

Document D1 discloses a process for the hydrocracking of feedstock such as crude oil residue, gas oil, ... (see D1: claim 1; Table 3; Example 3; column 6, lines 7-24) comprising

- a hydrocracking step, wherein said hydrocarbon feedstock is reacted with hydrogen under the same process conditions and the same catalyst as disclosed in D1 (claims 1, 4-7; Example 3); The terms "mixed oxide" and "solid solution" are considered to be equivalent.
- a distillation step for separating various fractionated compounds like middle distillates and unconverted heavier material (column 6, lines 7-24).

The Examining Division admits that the composition (paraffins content) of the feedstock is not mentioned in D1. However, since the feedstock can be a crude oil residue or a gas oil, it is likely that a considerable quantity of paraffins can be found in the feedstock.

The unconverted material obtained in the distillation step has an initial boiling point equal to or higher than 340°C, since the feedstock used in Example 3 has an initial boiling point of 354°C.

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/EP2004/006979

1.2

The following dependent Claims are also not new:

- **Claim 2:** see D1: claims 1, 4-6;
- **Claim 3:** see D1: claim 4;
- **Claim 8:** see D1: column 4, line 50 - column 5, line 14; claims 2 and 3;
- **Claim 9:** see D1: claims 2 and 3;
- **Claim 14:** see D1: Example 3;
- **Claim 15:** see D1: Example 3;
- **Claim 16:** see D1: Example 3;
- **Claim 18:** see D1: column 6, lines 7-24;

2. Inventive step

There is no evidence on file that the additional technical features of dependent **Claims 4, 5, 6, 7, 10, 11, 12, 13, 17, 19 - 25** might cause a technical effect. Consequently, it cannot be seen which technical problem is solved. Therefore, an inventive step cannot be acknowledged.

CLAIMS

1. A process for the contemporaneous preparation of middle distillates and lubricating bases starting from a feedstock comprising a mix of prevalently paraffinic hydrocarbons obtained by means of a synthesis process

5 from hydrogen and carbon monoxide, consisting for at least 30%, preferably at least 50%, of a high-boiling fraction with a distillation temperature higher than 360°C, comprising:

10 (i) at least one hydrocracking step, wherein said hydrocarbon mix is reacted with hydrogen at a temperature of between 200 and 450°C and a pressure of between 0.5 and 15 MPa, in the presence of a catalyst, for a time sufficient for converting at least 40% of

15 said high-boiling fraction, into a fraction of hydrocarbons which can be distilled at temperatures lower than 360°C;

20 (ii) at least one distillation step of the product of step (i) for separating at least a fraction of middle distillate and at least one high-boiling residue suitable for producing a lubricating base with an initial boiling point equal to or higher than 340°C, characterized in that said hydrocracking step (i) is effected in the presence of a supported catalyst comprising:

(A) a support of an acidic nature consisting of a catalytically active porous solid, including silicon, aluminum, phosphorus and oxygen bonded to one another in such a way as to form a mixed amorphous solid forming a single phase, characterized by an Si/Al atomic ratio of between 15 and 250, a P/Al ratio of at least 0.1, but lower than 5, a total pore volume ranging from 0.5 to 2.0 ml/g, an average pore diameter ranging from 3 nm to 40 nm, and a specific surface area ranging from 200 to 1000 m²/g;

(B) at least one metal with a hydro-dehydrogenating activity selected from groups 6 to 10 of the periodic table of elements, dispersed on said support (A) in an amount of between 0.05 and 5% by weight with respect to the total weight of the catalyst.

2. The process according to claim 1, wherein said active support of the catalyst has a total pore volume of between 0.7 and 1.7 ml/g, a surface area of between 300 and 900 m²/g and an average pore diameter of between 5 and 30 nm, an Si/Al ratio ranging from 20 to 200 and a P/Al ratio ranging from 0.3 to 3.5.
3. The process according to any of claims 1 and 2, wherein the difference between 10% and 90% in the distribution curve of the pore dimensions of said active support of the catalyst, is included within a diameter

range of between 2 and 40 nm.

4. The process according to any of the previous claims, wherein said catalyst includes, in addition to said active support (A), preferably in a mix therewith, a binder consisting of an inert inorganic solid.
5. The process according to the previous claim 4, wherein said inert binder is selected from silica, alumina, clay, titanium oxide (TiO_2) or zirconium oxide (ZrO_2), boron oxide (B_2O_3) or mixtures thereof.
- 10 6. The process according to any of the previous claims 4 or 5, wherein said binder is in an amount of 1 to 70% by weight, preferably 20 to 50% by weight, with respect to the weight of said inert binder and said amorphous support (A).
- 15 7. The process according to any of the previous claims 4 to 6, wherein said catalyst is in the form of pellets having dimensions of around 2-5 mm in diameter and 2-10 mm in length.
8. The process according to any of the previous claims, wherein said metal in component (B) of the catalyst is selected from nickel, molybdenum, tungsten, cobalt, platinum, palladium and mixtures thereof, preferably platinum and palladium.
- 20 9. The process according to any of the previous claims, wherein the concentration of said metal having a hy-

dro-dehydrogenating activity ranges from 0.2 to 1% by weight with respect to the total weight of said catalyst.

10. The process according to any of the previous claims,
5 wherein said feeding mix comprises a synthesis product of the Fischer-Tropsch type.
11. The process according to any of the previous claims,
wherein at least 80% by weight of said hydrocarbon mix
consists of paraffins.
- 10 12. The process according to any of the previous claims,
wherein said feeding mix consists for at least 80% by
weight of linear paraffins having from 5 to 80 carbon
atoms and an initial boiling point of between 45 and
675°C (by extrapolation).
- 15 13. The process according to any of the previous claims 1
to 11, wherein said feeding mix comprises from 40 to
80% by weight of a high-boiling fraction which can be
distilled at temperatures ≥ 360°C and from 20 to 60%
by weight of middle distillate.
- 20 14. The process according to any of the previous claims 1
to 11, wherein said feeding mix has an initial boiling
point of at least 260°C.
15. The process according to any of the previous claims,
wherein said hydrocracking step (i) is run at a tem-
25 perature of between 300 and 370°C and at a pressure of

- between 1 and 10 MPa, including the hydrogen pressure.
16. The process according to any of the previous claims, wherein said hydrocracking step (i) is effected with an initial (hydrogen)/(hydrocarbons) mass ratio of between 0.03 and 0.2.
- 5 17. The process according to any of the previous claims, wherein the α conversion in said hydrocracking step (i) ranges from 60 to 90%, preferably from 65 to 80%.
- 10 18. ~~The process according to any of the previous claims, wherein the high-boiling residue obtained in said step (ii) includes at least 80% by weight of an isomerized hydrocarbon mix.~~
- 15 18. 19. The process according to any of the previous claims, wherein an aliquot of said high-boiling residue obtained in said step (ii) is recycled to the hydrocracking step (i).
- 20 19. 20. The process according to any of the previous claims, wherein said high-boiling residue used for the production of lubricating bases is subjected to a dewaxing treatment.
- 20 21. The process according to claim 19, 20, wherein said dewaxing step consists of a catalytic dewaxing.
21. 22. The process according to any of the previous claims, comprising, in addition, a hydrogenating treatment of the feed to said hydrocracking step (i).
- 25

22. 23. The process according to any of the previous claims, wherein, before the hydrocracking step, a light fraction having a final boiling point lower than 380°C, preferably between 260 and 360°C, is separated from said feed, by distillation, before the hydro-cracking step.
- 5
23. 24. The process according to claim 22, 23, wherein said light fraction is subjected to a hydro-isomerization treatment in the presence of a suitable bi-functional catalyst with a hydro dehydrogenating activity to obtain an isomerized mix.
- 10
24. 25. The process according to claim 23, wherein said light fraction is subjected to a hydrogenating treatment, before the hydro-isomerization treatment.
- 15 25. 26. The process according to any of the previous claims 22 to 24 ~~23 to 25~~, wherein said light fraction or a product obtained therefrom, is joined to at least a part, preferably all, of said fraction of middle distillate obtained in step (ii) and sent to a fractionation step for the production of at least one fraction of middle distillate, preferably gas oil.
- 20